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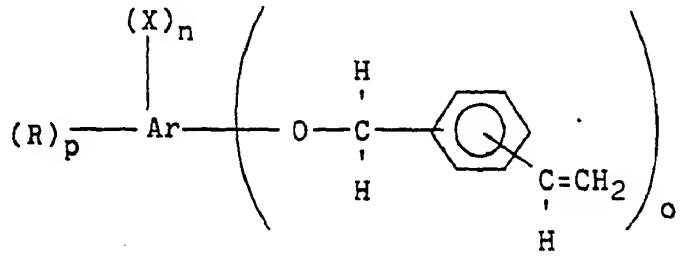
(54) Vinylbenzyl ethers of polyhydric halogenated phenolic compounds.

(57) The polyfunctional vinylbenzyl ethers of the formula:



(I)

wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety are prepared. These polyfunctional vinylbenzyl ethers can be copolymerized with polycyanate ester compounds to provide copolymers having dielectric constants below 3 and a V-0 rating in a UL-94 test.

EP 0 258 695 A1

VINYLBENZYL ETHERS OF POLYHYDRIC HALOGENATED PHENOLIC COMPOUNDS

This invention relates to monomers, polymers and copolymers of vinylbenzyl ethers of polyhydric halogenated phenolic compounds.

Vinyl-terminated compounds are useful in preparing a variety of both thermoset and thermoplastic resins. Additionally, such compounds are useful comonomers in a variety of resin system. The vinyl moieties are useful polymerization sites in free-radical induced and thermal-initiated polymerization reactions.

Aromatic nuclei are desirable included in the backbone of thermoset and thermoplastic resins because they provide both chemical and structural stability. Other useful moieties included in the backbones of such resins are halogens, such as bromine. The halogens are known to promote fire-resistance to compounds containing them.

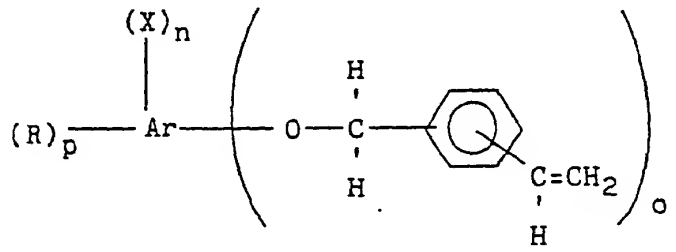
In the U.S. Patent 3,058,953, polymers and methods of preparing vinylbenzyl phenol ethers are disclosed. However, the monomers are monofunctional (i.e., they have only one vinyl moiety). In U.S. Patent 4,116,936, polymers of polyvinylbenzyl ethers of polyphenols are disclosed. However, the compounds which are halogenated require a glycidyl bridging group between aromatic rings. In U.S. Patent 4,180,680, methods for preparing halophenolvinylbenyzl ethers are disclosed. Unfortunately, the monomers are monofunctional.

An especially desirable family of thermoset resins is disclosed in U.S. Patent 4,528,366. These resins are aromatic polycyanate resins which can exhibit a dielectric constant of below 3 at 10 kHz. Therefore, these resins are desirably employed in preparing laminates for electronic circuit boards. Such polycyanates have been copolymerized with ethylenically unsaturated monomers in U.S. Patents 4,559,425 and 4,559,399. Other polycyanates have been copolymerized with maleimides and ethylenically unsaturated monomers, as described in U.S. Patents 4,371,689; 4,393,195; 4,396,745; and 4,469,859. Unfortunately, such compositions require expensive and complicated processing steps and fail to provide a polycyanate resin which exhibits the desired degree of fire retardancy.

In U.S. Patent 4,094,861, a non-inflammable polytriazene is disclosed. Unfortunately, such compounds do not exhibit as desirable physical properties of triazenes prepared with other polycyanates.

It would be desirable to have polyfunctional vinylbenzyl ethers of polyhydric halogenated phenolic compounds. It would further be desirable if such compounds could be copolymerized with other monomers, especially poly(arylcyanate) ester resins to impart fire-resistance to the cured compositions.

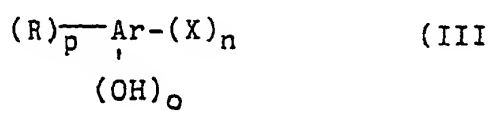
The present invention concerns a polyfunctional vinylbenzyl ether of the formula:



(I)

wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety;

said vinylbenzyl ether comprising a reaction product of a polyhydric halogenated phenolic compound of the formula:



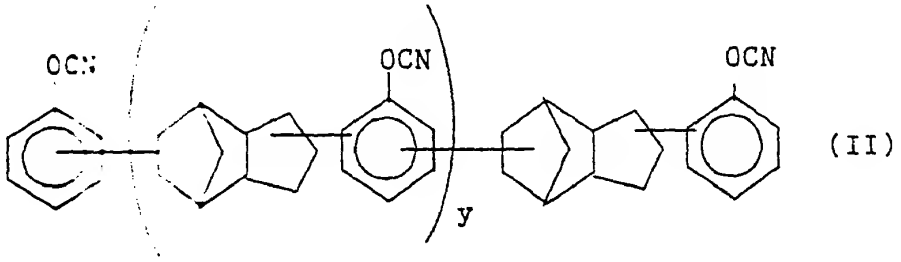
(III)

wherein Ar, X, R, n and o are as defined in Formula I;
p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties;
and an amount of vinylbenzyl chloride sufficient to provide at least 2 vinylbenzyl ether moieties per polyhydric phenolic compound.

Another aspect of this invention is a process for preparing polyfunctional vinylbenzyl ethers of polyhydric halogenated phenolic compounds corresponding to the above Formula (I). The process comprises contacting, under suitable reaction conditions, a polyhydric halogenated phenolic compound of Formula (III) with an amount of vinylbenzyl chloride sufficient to provide a reaction product having at least 2 vinylbenzyl ether moieties per phenolic compound.

In yet another aspect, this invention is a copolymer composition comprising a reaction product of the polyfunctional vinylbenzyl ether corresponding to the above Formula (I), and an ethylenically polymerizable comonomer.

In still yet another aspect, this invention is a copolymer composition comprising a reaction product of the polyfunctional vinylbenzyl ether corresponding to the above Formula (I), and an aromatic polycyanate ester compound. A preferred polycyanate ester compound is a dicyclopentadiene bridged polycyanate ester which corresponds to the formula



(II)

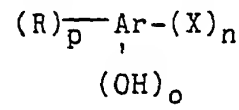
wherein y is greater than or equal to 0.

This invention provides polyfunctional vinylbenzyl ether compounds which are halogenated, and copolymers of such compounds. The vinylbenzyl ethers are useful for promoting certain properties in resins, such as fire resistance. The copolymers of the vinylbenzyl ethers and aromatic polycyanate ester compounds are useful in fabricating laminates useful for preparing electronic circuit boards. The neat resin employed in preparing the laminates exhibits a dielectric constant below 3, and a V-0 rating in the UL-94 test.

The polyhydric halogenated phenolic compounds useful in this invention are comprised of an aromatic nucleus substituted with at least 2 hydroxyl moieties (i.e., a polyhydric compound) and a halogen moiety. The aromatic nucleus contains from 6 to 24 carbons. The aromatic nucleus can be a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety. In addition to being substituted with the halogen and the hydroxyl moieties, the aromatic moieties can be substituted with a variety of substituents provided such substituents do not interfere with the etherification reaction or detract from the physical properties of the polymers or the copolymers. Examples of suitable substituents include alkyl moieties which are of a non-plasticizing length. Typically, alkyl chains of from 1 to 6 carbon atoms do not contribute a plasticizing effect and are suitable. Preferably, the aromatic nucleus is composed of two aromatic rings connected by a direct bond or an alkyl group.

Additionally, the aromatic nucleus is substituted with a halogen moiety. Preferred halogens are chlorine and bromine, with bromine being most preferred. Enough of the halogen is contained in the aromatic nucleus to provide the desired degree of fire retardancy to a copolymer composition containing the compounds of this invention. Typically, if the aromatic nucleus has a low halogen content, more of the comonomer will be required to provide the degree of fire retardancy. Contrariwise, if the aromatic nucleus contains a high halogen content less of the comonomers need to be employed. Preferably, such halogen amount provides a halogen content of at l ast 5 weight percent in the cured copolymer composition. Pr ferably, the aromatic nucleus is a polyhalogenated aromatic nucleus (i.e., contains more than one halogen moiety). Preferably, when the aromatic nucleus contains 2 bromine moieties per aromatic moiety, the bromine moieties are in a meta position on the aromatic moiety because the meta substituted bromines tend to provide a more stable compound.

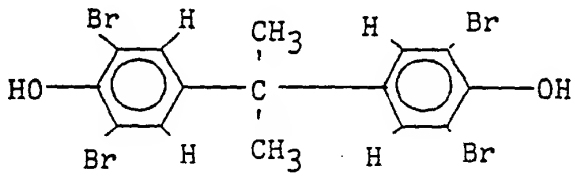
The polyhydric halogenated phenolic compound can correspond to the formula:



(III)

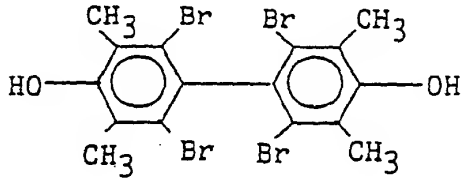
wherein
Ar, X, R, n and o are as defined in Formula I; and
p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties.

Preferred polyhydric halogenated phenolic compounds are polyhalogenated biphenols. An especially preferred biphenol is tetrabromobisphenol A corresponding to the formula:



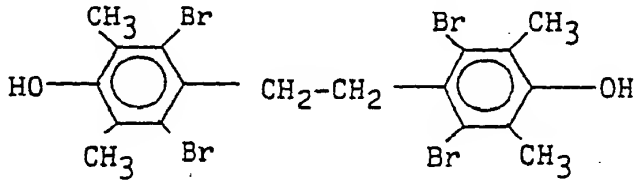
(IV)

Other preferred halogenated biphenol compounds include 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenyl which corresponds to the formula:



(V), and

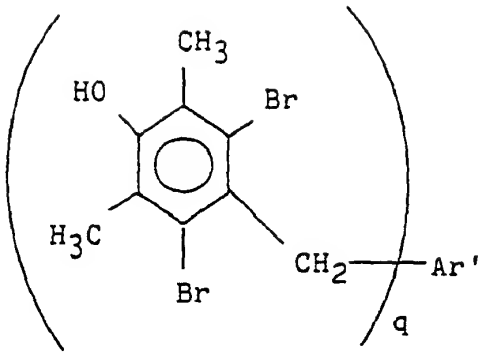
1,2-bis(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula



(VI)

These compounds can be prepared by contacting bromine and the respective poly(alkyl)polyhydroxy aromatic compound in the presence of a suitable brominating medium, such as using a Friedel-Crafts catalyst.

Still yet other preferred phenolic compounds are alkylated halogenated mesitols which correspond to the formula



(VII)

wherein Ar' is an aromatic nucleus of C_6-C_{24} carbon atoms which can be the same or different as Ar of Formula I and q is an integer of at least 2. A suitable method for preparing such a compound is a Friedel-Crafts alkylation wherein tribromomesitol is contacted with the desired aromatic compound in the presence of a suitable catalyst. Examples of such catalysts are Lewis and Bronsted acids such as $AlCl_3$, $AlBr_3$, and $FeCl_3$. Other suitable reaction conditions are temperatures ranging from 20° to 150°C, with higher temperatures producing a quicker reaction. The reaction is conducted at ambient pressures for any suitable time, which typically can range from 10 minutes to 14 hours. An inert diluent to solubilize the tribromomesitol can be employed. Haloalkanes such as dichloromethane can be employed. Tribromomesitol can be prepared according to the methods described in K. Auweis and F. Rapp, Ann., 302, 153-71 (1898); O. Jacobsen, Ann., 195, 265-92 (1879); and K. Fries and E. Brandes, Ann., 542 , 48-77 (1939).

Preferred polyhydric halogenated phenolic compounds are disclosed in and prepared by the methods described in U.S. Patent No. 4,621,159 issued November 4, 1986.

Vinylbenzyl chloride is readily available from The Dow Chemical Company and can be prepared according to known methods. Suitable methods are disclosed in U.S. Patents 2,780,604; 2,981,758; 3,311,602; Czechoslovakian Patent 83,721; British Patent 792,859; and Russian Patent 318, 560.

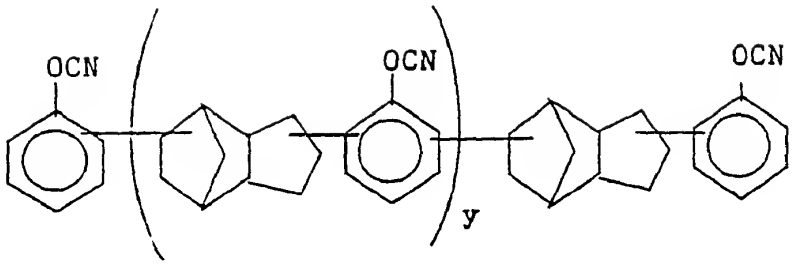
The polyfunctional vinylbenzyl ethers of the polyhydric halogenated phenolic compounds of this invention are prepared by contacting the polyhydric halogenated phenolic compounds with an amount of vinylbenzyl chloride sufficient to provide at least 2 vinylbenzyl ether moieties per phenolic compound. By "polyfunctional vinylbenzyl ethers" is meant that at least 2 vinylbenzyl ether moieties are provided per compound. The amount of vinylbenzyl chloride can be as much as one, and preferably is an excess of one vinylbenzyl chloride equivalent per hydroxyl equivalent in the phenolic compound. It is most advantageous to cap all the hydroxyl groups with vinylbenzyl groups because residual hydroxyl groups can detract from the polymer's and copolymer's properties. Preferably, the compounds of this invention are the reaction products (i.e., the isomeric mixture) of contacting only the vinylbenzyl chloride and 1 or more polyhydric halogenated phenolic compounds.

In one method, the polyhydric halogenated phenolic compound can be mixed with a solvent. An amount of base, for example potassium hydroxide, or sodium hydroxide, sufficient to initiate the reaction is added, and the mixture can then be heated. Finally, the desired amount of vinylbenzyl chloride is added, and the reaction product is recovered after cooling.

The vinylbenzyl ether compounds of this invention can be subjected to suitable polymerization conditions to provide polymeric compositions. Such suitable polymerization conditions include polymerizing in the presence of a suitable free-radical catalyst, or treating at suitable polymerization temperatures. Conventional vinyl polymerization reactions are suitable.

The polyfunctional vinylbenzyl ether of this invention can be copolymerized with other comonomers. Preferred comonomers include monomers which undergo ethylenically unsaturated polymerization reactions. For example, such comonomers include styrene, acylates and acrylic acid, ethylenically unsaturated hydrocarbons, maleimide compounds and the like. Other comonomers include the epoxy resins and the vinyl ester analogs of the epoxy resins.

A preferred comonom r useful in copolymerizing with the polyfunctional vinylbenzyl ethers of this invention are the aromatic polycyanate ester compounds described in U.S. Patent 4,528,366. An especially preferred aromatic polycyanate ester is the polyphenol cyanate ester bridged by a dicyclopentadiene moiety which corresponds to the formula



(VIII)

wherein y is greater than or equal to zero and is preferably 0:2.

The copolymers of the aromatic polycyanate ester and polyfunctional vinylbenzyl ether of this invention are prepared by melting the comonomers together and heating in the presence of a suitable trimerization catalyst. Examples of suitable catalysts are the cobalt salts. Especially preferred cobalt salts are cobalt naphthenate and cobalt acetylacetonate (CoAcAc).

The amount of the comonomers employed in preparing the copolymer can vary according to the types of properties desired in the copolymer. Increasing the amount of vinylbenzyl ether copolymer can increase the degree of fire resistance, but can be restricted by economical considerations. Typically, at least 8 weight percent, preferably at least 10 weight percent of the vinylbenzyl ether comonomer is employed. An especially preferred copolymer contains 12.2 weight percent of vinylbenzyl ether. Such a cured neat copolymer can exhibit a dielectric constant of below 3 at 10 kHz and a V-0 rating in a UL-94 test.

Laminates can be prepared by copolymerizing the aromatic polycyanate ester and the polyfunctional vinylbenzyl ether of this invention in the presence of suitable fillers. Examples of such fillers are organic and inorganic fibers and powders, such as glass fibers, Kevlar® fibers, and ceramic powders. The laminates are useful in preparing electronic circuit boards. The laminates prepared from the copolymers can exhibit a synergistic dielectric constant because the dielectric constant of the neat cured copolymerization product is lower than the dielectric constants of either of the cured homopolymers. Additionally, due to the presence of the bromine of the vinylbenzyl ether component, the laminates can provide a V-0 rating in the UL-94 test.

The following examples are provided to illustrate the invention.

Example 1 - The Preparation of Vinylbenzyl Ether of Tetrabromobisphenol A

A 1-liter 3-necked round bottom flask was fitted with a reflux condensor, a dropping funnel, and a mechanical stirrer. To the flask was added 12.85 g (0.32 moles) of sodium hydroxide and 400 ml of methanol. The mixture was stirred until the solid had dissolved. Tetrabromobisphenol A (87.34 g, 0.16 moles) was added to the flask and the material heated to 55°C. Vinylbenzyl chloride (54.10 g, 0.35 moles) was added dropwise over a period of 20 minutes. The mixture was maintained at 55°C for 400 minutes. The mixture was cooled and filtered to remove the solid which was a mixture of the reaction product and sodium chloride. The solid was slurried in 1,400 ml of a 1:1 mixture of methanol and water for 50 minutes and then filtered. The solid was rinsed with water and methanol and then dried in vacuo at 40°C to give 107 g of a white solid (98 percent yield). The product had a bromine content of 41 weight percent.

Example 2-Copolymerizing the Vinylbenzyl Ether of Tetrabromobisphenol A with Polycyanate Esters

An amount of the polycyanate ester of dicyclopentadiene was warmed to 100°C and poured into beakers. Different amounts of the vinylbenzyl ether of tetrabromobisphenol A were added and the mixture was stirred while heating to 90°C. A 1 percent, based on weight of cobalt, solution of cobalt acetylacetonate in acetontrile (100 parts per million cobalt) was added and the mixture was stirred well at 90°C. The mixture was degassed in a vacuum at 150°C for 10 minutes using carborundom boiling stones to aid in degassing. The material was poured into stainless steel parallel plate molds which were preheated to 125°C. The material was cured at 125°C for 1 hour, 175°C for 1 hour, 225°C for 1 hour and 250°C for 1 hour. The molds were allowed to cool slowly to 100°C and the plaques were removed.

Six samples of the copolymer composition having different amounts of the vinylbenzyl ether and aromatic polycyanate were prepared, and the degrees of fire resistance were measured according to the UL-94 test. The results are provided at Table I.

TABLE I

Sample	VBE(1) Content (Percent)	Br(2) Content (Percent)	Burn Time	UL-94 Rating
1	24.3	10	0	V-0
2	18.2	7.5	0	V-0
3(3)	12.2	5	23 sec.	V-0
4	9.7	4	67 sec.	V-1
5	7.3	3	>300 sec.	HB
6	4.9	2	>300 sec.	HB

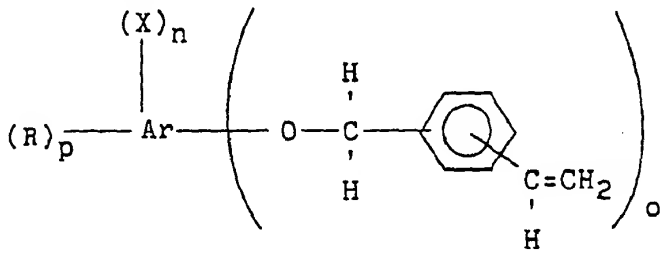
(1) Weight percent of bis(vinylbenzyl) ether of tetrabromobisphenol A in the copolymer.

(2) Weight percent of bromine in the copolymer.

(3) The dielectric constant of this sample, Sample 3, is 2.75, measured dry at 10 kHz.

Claims

1. A polyfunctional vinylbenzyl ether of the formula:



(I)

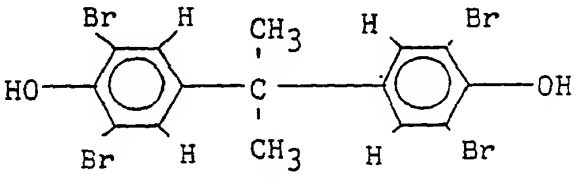
wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms, X is a halogen moiety, R is hydrogen or n alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety;
said vinylbenzyl ether comprising a reaction product of a polyhydric halogenated phenolic compound of the formula:

(III)

wherein Ar, X, R, n and o are as defined in Formula I;
p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties;
and an amount of vinylbenzyl chloride sufficient to provide at least 2 vinylbenzyl ether moieties per polyhydric phenolic compound.

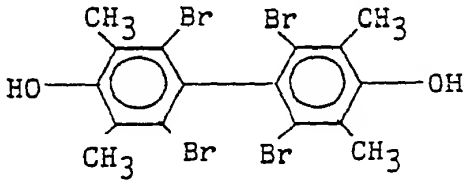
2. The vinylbenzyl ether of Claim 1, wherein the polyhydric halogenated phenolic compound is a polyhalogenated biphenol.

3. The vinylbenzyl ether of Claim 2 wherein the polyhalogenated biphenol is tetrabromobisphenol A which corresponds to the formula



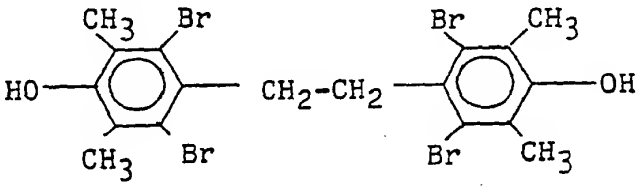
(IV)

4. The vinylbenzyl ether of Claim 2 wherein the polyhalogenated biphenol is 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenyl which corresponds to the formula



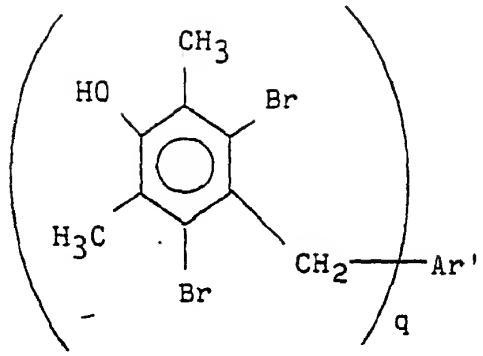
(V)

5. The vinylbenzyl ether of Claim 2 wherein the polyhalogenated biphenol is 1,2-bis-(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula



(VI)

6. The vinylbenzyl ether of Claim 1 wherein the polyhydric halogenated phenolic compounds is an alkylated halogenated mesitol which corresponds to the formula

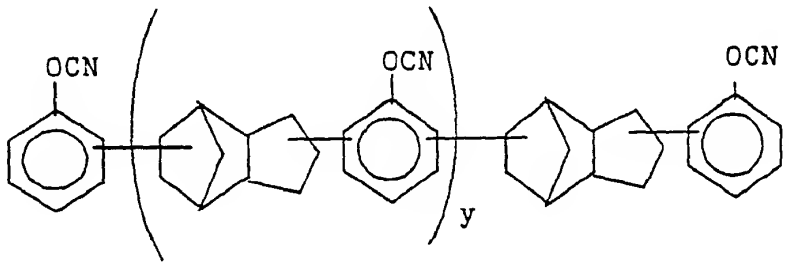


(VII)

wherein Ar' is an aromatic nucleus of C_6-C_{24} carbon atoms which can be the same or different as Ar of Formula I and q is an integer of at least 2.

7. A copolymer composition comprising a reaction product of a polyfunctional vinylbenzyl ether of Claim 1 and an aromatic polycyanate ester compound.

8. The copolymer composition of Claim 7, wherein the aromatic polycyanate ester compound is a dicyclopentadiene bridged polycyanate ester which corresponds to the formula



(VIII)

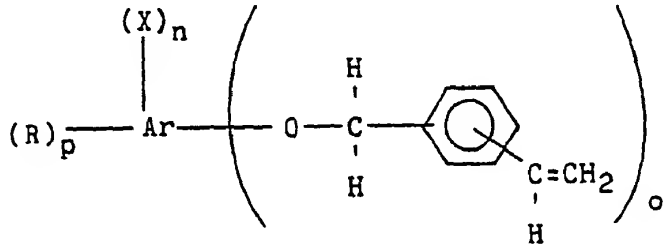
wherein y is 0.2.

9. The copolymer composition of Claim 8 wherein the copolymer composition exhibits a dielectric constant of less than 3 at 10 kHz, and a V-0 rating in a UL-94 test.

10. A copolymer composition comprising a reaction product of a polyfunctional vinylbenzyl ether of Claim 1 and an ethylenically polymerizable comonomer.

Claims for the following Contracting State : AT

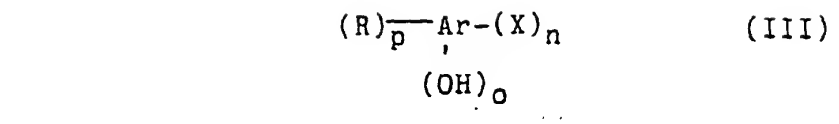
1. A process for the preparation of a polyfunctional vinylbenzyl ether of the formula:



(I)

wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety;
which process comprises contacting, under suitable reaction conditions, a polyhydric halogenated phenolic

compound of the formula:

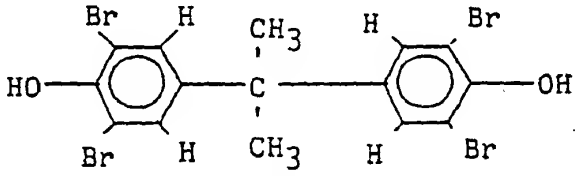


(III)

wherein Ar, X, R, n and o are as defined in Formula I;
p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties;
with an amount of vinylbenzyl chloride sufficient to provide a reaction product having at least two vinylbenzyl ether moieties per phenolic compound.

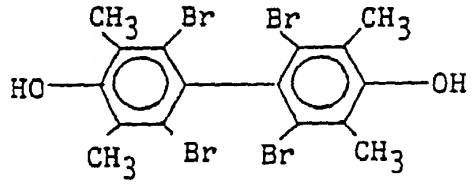
2. The process of Claim 1, wherein said polyhydric halogenated phenolic compound is a polyhalogenated biphenol.

3. The process of Claim 2 wherein the polyhalogenated biphenol is tetrabromobisphenol A which corresponds to the formula



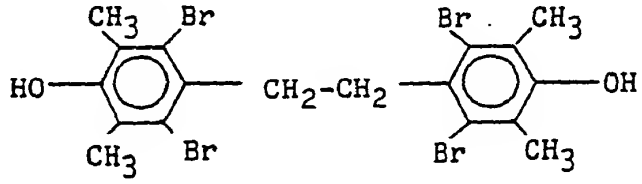
(IV);

3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenyl which corresponds to the formula



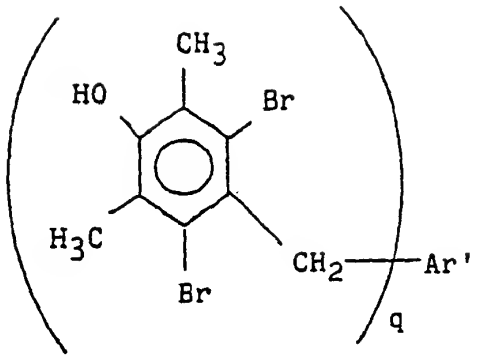
(V);

or 1,2-bis-(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula



(VI).

4. The process of Claim 1 wherein the polyhydric halogenated phenolic compound is an alkylated halogenated mesitol which corresponds to the formula



(VII)

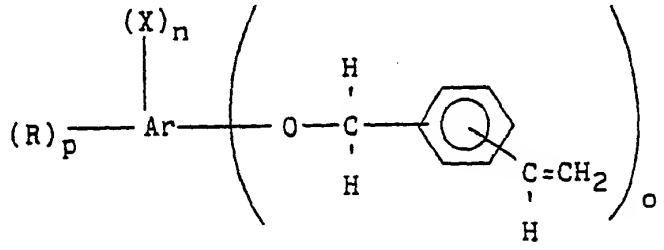
wherein Ar' is an aromatic nucleus of C_6-C_{24} carbon atoms which can be the same or different as Ar of Formula I and q is an integer of at least 2.

5. The process of any one of Claims 1 to 4 which is conducted in the presence of a solvent.

6. The process of any one of Claims 1 to 4 which is conducted in the presence of a suitable base.

7. The process of any one of Claims 1 to 4 which is conducted at an elevated temperature.

8. A process for the preparation of a copolymer composition which process comprises heating a polyfunctional vinylbenzyl ether of the formula:

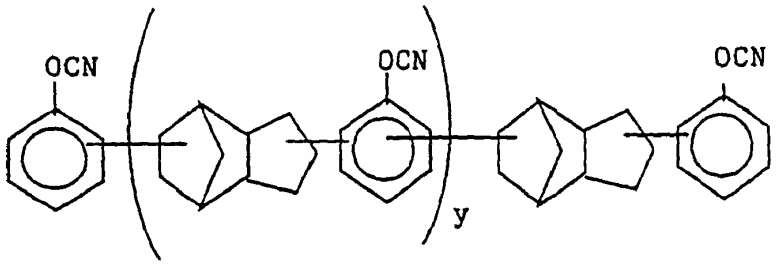


(I)

wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety;

with an aromatic polycyanate ester compound in the presence of a suitable trimerization catalyst.

9. The process of Claim 8 wherein the aromatic polycyanate ester compound is a dicyclopentadiene bridged polycyanate ester which corresponds to the formula



(VIII)

and the catalyst is cobalt naphthanate or cobalt acetylacetonate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 11 1655

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A,D	US-A-3 058 953 (E.L. McMASTER) * Whole document * ---	1-6,10	C 07 C 43/225 C 08 F 212/34 C 08 G 73/06
A,D	US-A-4 116 936 (E.C. STEINER) * Whole document * -----	1-6,10	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 C 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09-12-1987	WRIGHT M.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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